Density-functional theory and the v-representability problem for model strongly correlated electron systems

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Inspired by earlier work on the band-gap problem in insulators, we reexamine the treatment of strongly correlated Hubbard-type models within density-functional theory. In contrast to previous studies, the density is fully parametrized by occupation numbers *and* overlap of orbitals centered at neighboring atomic sites, as is the local potential by the hopping matrix. This corresponds to a good formal agreement between density-functional theory in real space and second quantization. It is shown that density-functional theory is formally applicable to such systems and the theoretical framework is provided. The question of noninteracting v representability is studied numerically for finite one-dimensional clusters, for which exact results are available, and qualitatively for infinite systems. This leads to the conclusion that the electron density corresponding to interacting systems of the type studied here is in fact *not* noninteracting v representable because the Kohn-Sham electrons are unable to reproduce the correlation-induced localization correctly.

I. INTRODUCTION

Originally formulated in the 1960s, density-functional theory (DFT) has since become the most widely used method for electronic-structure and total-energy calculations. It is a general theory that is applicable to finite molecular systems as well as to bulk solids and, unlike other computational methods, it has the distinct advantage of being *in principle* an exact theory that takes the electronic interaction fully into account. Density-functional theory is based on the observation that the total energy and other characteristic ground-state properties of a system of interacting electrons in an external potential can be considered as unique functionals of the one-particle density $n(\mathbf{r})$, which then replaces the wave functions as the basic variable.

Although potentially powerful, the original Hohenberg-Kohn theorem[1] does not provide a simple recipe to calculate the ground-state density of the interacting electron system, so that practical applications of density-functional theory rely on the Kohn-Sham scheme,[2] in which the interacting system is replaced by a fictitious system of noninteracting electrons with the same spatial density moving in an effective potential. The central *assumption* is that such an equivalent system of noninteracting electrons always exists, i. e., that all interacting v representable densities are also noninteracting v representable.

In the Kohn-Sham scheme, the total energy is split into several contributing functionals, all but one of which are either known explicitly or can be replaced by other well-known terms. The essential unknown quantity is the exchange-correlation energy $E_{\mathrm{xc}}[n]$, a universal functional of the density, and its functional derivative, the exchange-correlation potential $V_{\mathrm{xc}}([n];\mathbf{r})$.

Although, unfortunately, the exact analytic expression for the exchange-correlation energy remains unknown, many properties of the functional have been cataloged.[3] One of the more surprising features is a finite discontinuity in the exchange-correlation potential with respect to particle number,[4] which has the effect that even exact density-functional theory will underestimate the band gap of semiconductors. The question whether the poor agreement between density-functional calculations and the true band gap is indeed mainly due to this discontinuity or rather to additional approximations such as the local-density approximation (LDA) is known in the literature as the band-gap problem.

The Hubbard model, a simple second-quantization model for strongly correlated electrons, may be solved exactly for small clusters and so could be used to explore the properties of exact density-functional theory. This was done by Gunnarsson and Schönhammer in a study of the band-gap problem[5] and subsequently for comparing the Kohn-Sham Fermi surface with the exact quasiparticle Fermi surface.[6] In their second-quantization version of density-functional theory, the density is replaced by the occupation numbers only and the place of the external potential is taken by the diagonal on-site energies, whereas all nondiagonal hopping parameters are treated as constants. This is a consistent approach to correlated systems, but it does not follow the second quantization of the operators in question.

In this paper, we investigate a different formulation of density-functional theory for correlated Hubbard-type systems that is closer to the original scheme in the continuum. Our approach is strictly based on second quantization with a complete parametrization of the density, which includes the overlap between orbitals centered at different atomic sites, and no constraints on the local potential. We demonstrate that density-functional theory, in this formulation, is *in principle* applicable to the Hubbard model, but we also show that the ground-state density is in fact *not* noninteracting v representable

under the Kohn-Sham scheme. These findings should be of particular interest since the results of the above-mentioned model calculations have often been cited in connection with the properties of real-space functionals, especially the band-gap problem:[7] Gunnarsson and Schönhammer found that the discrepancy between the true band gap and the energy-eigenvalue gap derived by density-functional theory using the LDA was mainly due to the LDA itself rather than to the discontinuity in the exchange-correlation potential; the opposite was found in a study of more realistic semiconductor models by Godby, Schlüter and Sham.[8]

In Section II we will establish a formulation of density-functional theory appropriate for the Hubbard model and prove the fundamental theorems. In Section III we will examine the influence of correlation and the external potential on the density and highlight the importance of overlap between orbitals centered at different sites. In Section IV we will discuss the question of v representability and demonstrate that the ground-state density of the interacting Hubbard model and of related models is *not* noninteracting v representable.

II. FORMALISM

A. The Hubbard model

The Hubbard Hamiltonian[9] is given by

$$\hat{H} = \sum_{\langle ij \rangle} \sum_{\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \tag{1}$$

The index i labels the atomic sites and the summation over $\langle ij \rangle$ includes all pairs up to nearest neighbors. $\sigma \in \{\uparrow, \downarrow\}$ denotes the two spin orientations.

The first part of the Hamiltonian represents the contribution due to the kinetic energy and the external (pseudo)potential $V_{\rm ext}(\mathbf{r})$ and is responsible for the electrons hopping between the atomic sites. $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are the creation and annihilation operators for an electron at site i with spin σ, respectively. The hopping-matrix elements t_{ij} are real and satisfy the symmetry condition $t_{ij} = t_{ji}$. They are the representation of the external potential in second quantization and are related to it by

$$t_{ij} = \int \phi^*(\mathbf{r} - \mathbf{R}_i) \left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\rm ext}(\mathbf{r}) \right) \phi(\mathbf{r} - \mathbf{R}_j)\, d\mathbf{r}, \tag{2}$$

where $\phi(\mathbf{r} - \mathbf{R}_i)$ is the Wannier-type orbital centered at $\mathbf{R}_i$ of the system in question. The existence of these orbitals underlies second quantization, but their actual analytic form is of no consequence for the numerical work presented below.

The second contribution to the Hamiltonian represents the on-site Coulomb repulsion, which acts between two electrons occupying the same atomic site. $\hat{n}_{i\sigma} \equiv c_{i\sigma}^{\dagger} c_{i\sigma}$ is the particle-number operator for site i and spin σ. The interaction parameter U is real and $U > 0$. Its value is given by

$$U = \frac{1}{2} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{|\phi(\mathbf{r})|^2 \, |\phi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}'. \tag{3}$$

When discussing the adjusted density-functional formalism in this section, we will always refer to the Hubbard Hamiltonian in the general form (1) without specifying the dimensionality or configuration of the system. In particular, no spatial symmetries are assumed, so the formalism holds for lattices as well as for finite or disordered systems. In the latter case, the occurence of different Wannier orbitals may lead to a site-dependent interaction parameter, but this is not in conflict with the general formalism. M denotes the number of sites and N is the number of electrons.

As a prerequisite of density-functional theory, it is essential to define the density in a proper way. As for the Hamiltonian, we assumed that overlap of the Wannier orbitals was negligible except between neighboring sites, and this assumption must be retained for consistency. The density corresponding to some state $|\Psi\rangle$ will therefore be of the general form

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \sum_{\langle ij \rangle} n_{ij} \phi^*(\mathbf{r} - \mathbf{R}_i) \phi(\mathbf{r} - \mathbf{R}_j). \tag{4}$$

The density operator $\hat{n}(\mathbf{r})$ is given by

$$\hat{n}(\mathbf{r}) = \sum_{\langle ij \rangle} \sum_{\sigma} \phi^*(\mathbf{r} - \mathbf{R}_i) \phi(\mathbf{r} - \mathbf{R}_j) c_{i\sigma}^{\dagger} c_{j\sigma} \tag{5}$$

in second quantization and the density is thus parametrized by the coefficients

$$n_{ij} = \sum_{\sigma} \langle \Psi | c_{i\sigma}^{\dagger} c_{j\sigma} | \Psi \rangle. \tag{6}$$

The diagonal elements $n_i \equiv n_{ii}$ are just the orbital occupation numbers, but we are also left with off-diagonal elements. Strictly speaking, the dependence of the total energy on the density coefficients is that of a function rather than a functional, but for clarity, we will continue talking about density functionals. It should then be borne in mind that all densities to be considered are of the form (4).

B. The Hohenberg-Kohn theorem

The analog of the Hohenberg-Kohn theorem in this formalism incorporates three important statements.

(i) The ground-state expectation value of any observable $\hat{O}$ is a unique functional $O[n^{\rm GS}]$ of the ground-state electron density $n^{\rm GS}$.

(ii) The ground-state density $n^{\rm GS}$ minimizes the total-energy functional $E[n]$.

(iii) The total-energy functional can be written in the form

$$E[n] = F[n] + \sum_{\langle ij \rangle} t_{ij} n_{ij} \tag{7}$$

where $F[n]$ is a *universal* functional of the density.

In proving these statements, we have largely followed the procedure given by Levy.[10] Throughout, the ground state is assumed to be nondegenerate, but the formalism can be extended to cover degenerate ground states in much the same way as conventional density-functional theory.[11] First, we define the energy functional by

$$E[n] := \min_{|\Psi\rangle \to n} \langle \Psi | \hat{H} | \Psi \rangle. \tag{8}$$

The constraint $|\Psi\rangle \to n$ marks all antisymmetric N-body wave functions that yield the density n as defined above. This functional is properly defined for all N-representable densities, i. e., all densities that can be constructed from N-fermion wave functions. In particular, this includes all ground-state densities studied here. The variational principle then guarantees that the ground-state density indeed minimizes $E[n]$.

At the same time, the definition (8) constitutes a map $n^{\rm GS} \mapsto |\Psi[n^{\rm GS}]\rangle$, where $|\Psi[n^{\rm GS}]\rangle$ denotes the N-body wave function that yields the ground-state density $n^{\rm GS}$ of a particular system and minimizes the energy. We can therefore properly define the ground-state expectation value of an arbitrary observable $\hat{O}$ as a functional of the ground-state density by

$$O[n^{\rm GS}] := \langle \Psi[n^{\rm GS}] | \hat{O} | \Psi[n^{\rm GS}] \rangle. \tag{9}$$

The single-particle contribution to the functional $E[n]$, which we will henceforth term the hopping energy, can be essentially simplified. Using the explicit form of the Hubbard Hamiltonian and the definition of the density coefficients, (8) can be transformed into the expression

$$E[n] = \sum_{\langle ij \rangle} t_{ij} n_{ij} + \min_{|\Psi\rangle \to n} \left\langle \Psi \left| U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \right| \Psi \right\rangle. \tag{10}$$

We can now define the observable $\hat{F}$ by

$$\hat{F} := U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \tag{11}$$

and thereby obtain the form (7). $F[n]$ is universal in the sense that it is independent of the particle number and the external potential. The upper limit in the sum over i need not be specified because the number of sites enters through the constrained search over the wave functions that yield the density n. Finally, the interaction U is fixed through its definition (3). This completes the proof of the Hohenberg-Kohn theorem.

C. The Kohn-Sham scheme

The second part of the Hohenberg-Kohn theorem suggests that if we knew the exact analytic form of $E[n]$, we could find the ground-state energy by a variational principle that minimizes the functional under the constraint of particle conservation, but it does not provide a practical procedure to do so. Rather, the constrained search over the wave functions leaves us with another complicated N-body theory.

The essential simplification is obtained by the Kohn-Sham scheme, which *assumes* that the ground-state density $n^{\rm GS}$ of the Hamiltonian (1) can alternatively be generated by the ground state of a fictitious system of noninteracting electrons moving in an effective potential. This is known as the assumption of noninteracting v representability. The equivalent system can be used to calculate the exact ground-state energy and the mathematical expense is reduced to an effective one-particle problem. This one-particle Hamiltonian is given by

$$\hat{H}_s = \sum_{\langle ij \rangle} \sum_\sigma t_{ij}^{\rm eff} c_{i\sigma}^\dagger c_{j\sigma}. \tag{12}$$

The N-body ground state is supposed to be nondegenerate. Following the central assumption stated above, the hopping parameters are chosen so that the ground-state density matches that of the interacting system. In this case, the density coefficients are given by

$$n_{ij}^{\rm GS} = \sum_{\gamma=1}^{N} \sum_\sigma \langle \psi_\gamma | c_{i\sigma}^\dagger c_{j\sigma} | \psi_\gamma \rangle \tag{13}$$

in terms of the one-particle wave functions that correspond to the N lowest energy eigenvalues ϵ_γ of $\hat{H}_s$. The ground-state energy of the noninteracting system is a functional of $n^{\rm GS}$ and can be written directly as

$$E_s[n^{\rm GS}] = \sum_{\gamma=1}^{N} \epsilon_\gamma = \sum_{\langle ij \rangle} t_{ij}^{\rm eff} n_{ij}^{\rm GS}. \tag{14}$$

Due to the Hohenberg-Kohn theorem, this functional has to be stationary under infinitesimal density variations δn within the domain of valid N-fermion densities:

$$0 = \delta E_s = \sum_{\langle ij \rangle} t_{ij}^{\rm eff} \delta n_{ij}. \tag{15}$$

In order to map the interacting electrons onto the noninteracting system, we start by separating a Hartree term out of the total-energy functional (8):

$$E[n] = \sum_{\langle ij \rangle} t_{ij} n_{ij} + \frac{U}{2} \sum_i n_i^2 + E_{\rm xc}[n]. \tag{16}$$

The exchange-correlation functional $E_{\rm xc}[n]$ incorporates all exchange and correlation effects that are not included in the Hartree term and is formally defined by

$$E_{\rm xc}[n] := F[n] - \frac{U}{2}\sum_i n_i^2. \qquad (17)$$

At the ground-state density, $E[n]$ must also be stationary under infinitesimal variations δn that correspond to N-fermion densities:

$$0 = \delta E = \sum_{\langle ij\rangle} \left(t_{ij} + U\delta_{ij} n_i^{\rm GS} + v_{ij}^{\rm xc}[n^{\rm GS}]\right) \delta n_{ij}, \qquad (18)$$

where $v_{ij}^{\rm xc}[n^{\rm GS}]$ denotes the elements of the exchange-correlation matrix, which is defined by

$$v_{ij}^{\rm xc}[n^{\rm GS}] := \left.\frac{\partial E_{\rm xc}[n]}{\partial n_{ij}}\right|_{n=n^{\rm GS}}. \qquad (19)$$

By comparison with (15), the effective hopping-matrix elements can now be uniquely defined as

$$t_{ij}^{\rm eff} := t_{ij} + U\delta_{ij} n_i^{\rm GS} + v_{ij}^{\rm xc}[n^{\rm GS}]. \qquad (20)$$

This expression for the effective potential can be used to calculate the ground-state electron density in a self-consistent manner. The total energy can eventually be calculated from (16). As usual, it is possible to replace the term that contains the kinetic energy using the eigenvalues ϵ_γ of the one-particle Schrödinger equation, but this is not advisable here because the hopping term is already of the simplest possible form.

In principle, splittings of the total energy other than (16) are possible. In Ref. 5 the hopping term is treated much like the kinetic energy in the conventional formalism. Hence the functional $E[n]$ splits into the hopping energy of the corresponding system with $U = 0$, the Hartree term, and an exchange-correlation energy defined in a different way from the one used here. However, only the formulation introduced here shows the distinct feature that the term $F[n]$ is a *universal* functional independent of the external potential, in practice a prerequisite for any systematic application of density-functional theory, and a feature of density-functional theory for real systems. We therefore believe that our formulation of density-functional theory is the natural counterpart of that used for *ab initio* calculations.

D. The problem of v representability

The conceptual idea of the Kohn-Sham scheme, constructing the ground-state density by means of a system of noninteracting electrons, ultimately leads to the question of v representability. As a definition, we call a density interacting v representable if it corresponds to the ground state of a Hamiltonian of the form (1), which includes a specified on-site interaction term. On the other hand, a density that corresponds to the ground state of a one-particle Hamiltonian of the form (12) is called noninteracting v representable.

The functionals in second quantization differ from those in the continuum formulation and we cannot hope to transfer any previous findings on the question of v representability. The constrained search guarantees that all functionals are well defined for arbitrary N-representable densities, which includes both interacting and noninteracting v representable densities, but the crucial question is whether the ground-state density of a given interacting system indeed minimizes a corresponding Kohn-Sham energy functional $E_s[n]$. As there is no obvious indication whether the two domains of interacting and noninteracting v representable densities overlap or even coincide, we have investigated this question by means of numerical simulations and we have come to the conclusion that they are in fact largely distinct.

III. CORRELATION AND THE OVERLAP COEFFICIENTS

A. The effect of correlation

We consider a finite one-dimensional Hubbard chain at half-filling, which we solve numerically by exact diagonalization. We assume the on-site energies $e_i \equiv t_{ii}$ to be zero and the other hopping parameters to be identical between all nearest neighbors:

$$\hat{H} = -t\sum_{i=1}^{M-1}\sum_\sigma \left(c_{i\sigma}^\dagger c_{(i+1)\sigma} + c_{(i+1)\sigma}^\dagger c_{i\sigma}\right) + U\sum_{i=1}^{M} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \qquad (21)$$

with $t > 0$. We give results for an eight-site chain here, a configuration that has a nondegenerate ground state for all choices of t and U. Calculations performed for other chain lengths have produced very similar results.

To visualize the effect of correlation, we fix $t = 1$ and calculate the ground-state energy and the density coefficients for different U. The results are shown in Table I. The total energy $E(U)$ is the lowest eigenvalue of the Hamiltonian matrix, $T(U) = -t\sum_{i=1}^{M-1}(n_{i(i+1)} + n_{(i+1)i})$ denotes the hopping energy and $E_H(U) = U\sum_{i=1}^{M} n_i^2/2$ is the Hartree energy. The exchange-correlation energy is calculated from $E_{\rm xc}(U) = E(U) - T(U) - E_H(U)$.

We find that the occupation numbers $n_i = 1$ exactly, independent of U: the electrons are distributed evenly. On the other hand, the interaction obviously reduces the overlap between orbitals centered at different sites. The underlying physical reason is that the on-site Coulomb repulsion opposes the hopping of electrons to a site that is already occupied. The correlation thus reduces the electron fluctuations. For increasing U, the electrons become eventually localized on the atomic sites and the hopping energy approaches zero.

The localization effect that we have visualized here is just the mechanism that is responsible for the Mott

TABLE I. Energy and density coefficients of the eight-site Hubbard chain for $t = 1$ and selected values of U. The increasing correlation reduces the overlap and thus leads to a strong localization of the electrons. In the limit $U \to \infty$, the orbital overlap reaches zero and the electrons are completely localized.

	$U = 0$	$U = 2$	$U = 4$	$U = 8$	$U \to \infty$
$E(U)$	-9.52	-6.23	-4.24	-2.42	0.00
$T(U)$	-9.52	-8.82	-7.19	-4.59	0.00
$E_H(U)$	0.00	8.00	16.00	32.00	∞
$E_{\rm xc}(U)$	0.00	-5.41	-13.05	-29.83	$-\infty$
$n_1 = n_8$	1	1	1	1	1
$n_2 = n_7$	1	1	1	1	1
$n_3 = n_6$	1	1	1	1	1
$n_4 = n_5$	1	1	1	1	1
$n_{12} = n_{78}$	0.862	0.793	0.641	0.408	0.000
$n_{23} = n_{67}$	0.495	0.455	0.370	0.238	0.000
$n_{34} = n_{56}$	0.758	0.714	0.589	0.376	0.000
n_{45}	0.529	0.484	0.391	0.249	0.000

metal-insulator transition,[12] although it has been shown that a true phase transition does not occur for finite U: the half-filled Hubbard chain is a conductor for $U = 0$ and a Mott insulator otherwise.[13]

B. The importance of the overlap parameters

The possibility of electrons hopping between neighboring atomic sites requires a significant overlap of the orbitals. On the mathematical side, this overlap explicitly enters the expression for the hopping parameters (2). It is therefore both qualitatively and quantitatively an important feature of the system. For reasons of consistency, one must use overlap coefficients as well as occupation numbers to parametrize the density. On the other hand, it might be argued that the overlap contribution to the density in real space was negligible due to the strong localization of the Wannier-type orbitals. Although this argument might seem plausible if the Wannier states are chosen to resemble the localized d orbitals found in transition metals, there is more to be said: the energy as a functional of the density depends very sensitively on the overlap coefficients and it is therefore essential to include those in all practical applications. To clarify this point, we now hold the parameter $U = 4$ fixed and vary t. Results are given in Table II. The density coefficients are the same as in Table I, because they depend on the ratio t/U only.

As the interaction is now specified by fixing U, all energy expectation values are unique functionals of the density due to the Hohenberg-Kohn theorem. The important point to note is that for this particular configuration, the occupation numbers are identical regardless of the external potential represented by t, *but the overlap coefficients are not*, which allows us to identify their influence. As for the hopping energy, the dependence on the overlap is known explicitly:

$$T[n] = -t \sum_{i=1}^{M-1} \left(n_{i(i+1)} + n_{(i+1)i} \right). \qquad (22)$$

The exchange-correlation energy $E_{\rm xc}[n]$ also varies, but its dependence on the overlap is much more subtle. When applying the Kohn-Sham scheme, whether in exact or approximate density-functional theory, we must thus make sure to reproduce both the exact occupation numbers *and* overlap coefficients of the interacting system.

In the formalism used in Ref. 5, $T[n]$ is equal to the hopping energy of the corresponding system with zero interaction and would therefore be proportional to t, whereas the Hartree term is constant if the occupation numbers are. The sum of both then changes linearly with t. However, from the values given in Table II, it is clear that the total energy is not linear. The exchange-correlation energy must therefore depend sensitively on t, which is treated as a parameter. If an analytic approximation is used rather than the exact functional, it should definitely show this feature. It is then clear that an approximation such as the "local-density approximation" defined by Eq. (2) in Ref. 5, which depends only on U and on the occupation numbers and so is independent of t, has a fundamental flaw not shared by the normal LDA for real systems. Results that depend on making a connection between such an approximation and the LDA for real systems, such as the conclusions of Ref. 5 regarding the LDA band-gap error, are therefore questionable.

TABLE II. Energy and density coefficients of the eight-site Hubbard chain for $U = 4$ and selected values of t. As the occupation numbers remain constant, the change in the energy values reflects the dependence of the functionals on the non-diagonal density coefficients.

	$t \to \infty$	$t = 2$	$t = 1$	$t = 0.5$	$t = 0$
$E[n]$	$-\infty$	-12.45	-4.24	-1.21	0.00
$T[n]$	$-\infty$	-17.64	-7.19	-2.29	0.00
$E_H[n]$	16.00	16.00	16.00	16.00	16.00
$E_{\rm xc}[n]$	-8.00	-10.81	-13.05	-14.92	-16.00
$n_1 = n_8$	1	1	1	1	1
$n_2 = n_7$	1	1	1	1	1
$n_3 = n_6$	1	1	1	1	1
$n_4 = n_5$	1	1	1	1	1
$n_{12} = n_{78}$	0.862	0.793	0.641	0.408	0.000
$n_{23} = n_{67}$	0.495	0.455	0.370	0.238	0.000
$n_{34} = n_{56}$	0.758	0.714	0.589	0.376	0.000
n_{45}	0.529	0.484	0.391	0.249	0.000

IV. RESULTS AND DISCUSSION

A. Numerical studies for small M

In order to test the existence of effective hopping parameters and thereby decide the question of noninteracting v representability, we set up a trial Hamiltonian matrix and use iterative nonlinear optimization techniques to vary the effective on-site energies and nearest-neighbor hopping parameters so as to reproduce as closely as possible the density coefficients of the interacting electron system. Occupation numbers and nearest-neighbor overlap coefficients are taken into account. Both the potential and the density are thus characterized by two parameters per site. Considering the complete Hamiltonian (21), we can obtain an initial guess by setting $U = 0$. Table I indicates that the corresponding densities are relatively close and we can therefore safely assume this to be a good starting point. The eigenstates of the one-particle Hamiltonian $\hat{H}_s$ are calculated by exact diagonalization. We have checked that the optimization is stable and insensitive to any reasonable choice of the initial guess.

We judge the quality of an approximation to the true density by summing the squared deviations between the approximate and the true density coefficients. Only the M independent coefficients are considered; the rest is determined by the intrinsic symmetry $n_{ij} = n_{ji}$ and the spatial symmetry with respect the center of the chain. As the hopping parameters satisfy the same symmetry conditions, only M are in fact independent.

The results of the optimization for the half-filled eight-site chain with $t = 1$ and $U = 4$ are shown in Table III, where we give the respective on-site energies and hopping parameters and compare the density of the best-fit Kohn-Sham system with the true density of the interacting system and that of the initial trial Hamiltonian with $t = 1$ and $U = 0$. Although the Kohn-Sham system gives the correct occupation numbers n_i, it is evidently *unable to reproduce the correct overlap coefficients* and thereby simulate the localization effect: the density is *not* noninteracting v representable. In fact, the overall quality of the approximation to the density, given by the sum of the deviation squares *SUMSQ*, is only little better than the approximation that is obtained by simply neglecting the interaction in the first place and setting $U = 0$.

It is interesting to note that the Kohn-Sham system approaches the true density best at the ends of the chain, whereas towards the center, it is little different from the density of the $U = 0$ system. This fact is reflected by the effective hopping parameters: towards the ends of the chain, they drop substantially to approach the atomic limit, which effectively reduces the overlap. It is this contribution that is responsible for the decrease of *SUMSQ* in the first place. In the center of the chain, however, the hopping parameters are almost constant and the density resembles that of the $U = 0$ system.

In Fig. 1 we compare the real-space density of the Kohn-Sham system with that of the interacting system. The increasing deviation towards the center of the chain is clearly visible. We have used real symmetric orbitals based on trigonometric functions for the purpose of this visualization only. These assume a maximum at the position of the atom, have one zero at either side, and extend to the nearest-neighbor atom. The main numerical work is, of course, independent of a specific choice of orbitals.

Although we are using a nonlinear optimization routine, the chances of finding a solution will depend on the ratio of independent variables to residual functions. Multiplying the Hamiltonian by an arbitrary factor or adding a constant to the on-site energies only affects the eigenvalues but leaves the eigenstates and thereby the density coefficients unchanged. For this reason, the overlap throughout the chain cannot be lowered by generally choosing smaller hopping parameters. Also, because of these two degrees of freedom in the hopping matrix, the number of relevant variables is in fact just $M-2$ instead of M. As for the target density coefficients, one is trivially determined by the requirement that the occupation numbers n_i add up to N. Besides, the density must be constructable from the wave function of N interacting electrons, but this imposes complicated nonlinear relations that can be expected to be of no relevance for the optimization procedure. The number of effectively independent residual functions is therefore reduced by just one to $M-1$ and so exceeds the number of free variables.

TABLE III. Hopping parameters, scaled so that $t_{45} = -1$, and density of the Kohn-Sham system (KS) compared with the original system with ($U = 4$) and without ($U = 0$) interaction for the eight-site Hubbard chain. The nonzero deviation between the overlap coefficients corresponding to $U = 4$ and KS, also represented by *SUMSQ*, indicates that the density of the interacting electron system is *not* noninteracting v representable.

	$U = 4$	KS	$U = 0$
$e_1 = e_8$	0	0	0
$e_2 = e_7$	0	0	0
$e_3 = e_6$	0	0	0
$e_4 = e_5$	0	0	0
$t_{12} = t_{78}$	-1	-0.027	-1
$t_{23} = t_{67}$	-1	-0.255	-1
$t_{34} = t_{56}$	-1	-1.021	-1
t_{45}	-1	-1.000	-1
$n_1 = n_8$	1	1	1
$n_2 = n_7$	1	1	1
$n_3 = n_6$	1	1	1
$n_4 = n_5$	1	1	1
$n_{12} = n_{78}$	0.641	0.648	0.862
$n_{23} = n_{67}$	0.370	0.428	0.495
$n_{34} = n_{56}$	0.589	0.819	0.758
n_{45}	0.391	0.503	0.529
SUMSQ		0.069	0.112

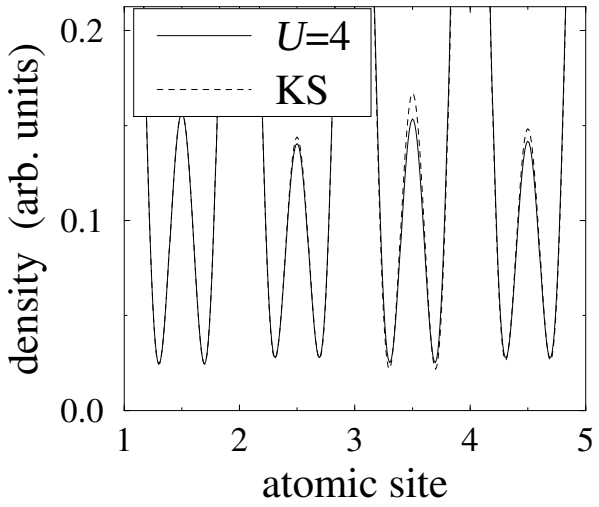

FIG. 1. Electron density of the eight-site Hubbard chain ($U = 4$) together with that of the Kohn-Sham system that reproduces it as closely as possible (KS), visualized by assuming a particular form of orbitals (see the text). There is good agreement at the ends of the chain (site 1), but increasing deviation towards the center (site 5). The deviation illustrates the fact that the density of the interacting system is *not* noninteracting v representable.

From a purely mathematical point of view, the nonexistence of an effective potential is thus not surprising.

We have performed calculations for different chain lengths and always obtained similar results. In conclusion, we note that in the case of small M, the density of the one-dimensional Hubbard chain is *not* noninteracting v representable because the Kohn-Sham system is unable to simulate the increased localization of the electrons. This is a systematic feature and will hold for all nonzero U.

B. The limit $M \to \infty$

The infinite chain is translationally invariant. The Hamiltonian of the interacting electron system must therefore be of the form

$$\hat{H} = -t \sum_{i=-\infty}^{\infty} \sum_{\sigma} \left(c_{i\sigma}^{\dagger} c_{(i+1)\sigma} + c_{(i+1)\sigma}^{\dagger} c_{i\sigma} \right) + U \sum_{i=-\infty}^{\infty} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \tag{23}$$

Without performing numerical calculations, we can conclude from our previous studies that the interaction will lead to a certain reduction of the overlap and to an increased localization of the electrons. In any case, the density of the interacting system will be different from the density that we obtain after dropping the interaction term in the Hamiltonian.

As for the noninteracting Kohn-Sham system, the translational invariance requires that the effective on-site energies and hopping parameters are constant throughout the chain. This leaves just two variables, a uniform e^{eff} and t^{eff}. However, these are related to the two trivial transformations described above that leave the eigenstates unchanged; their values do not affect the density and may be scaled to zero and $-t$. As a consequence, the electron density of the Kohn-Sham system must necessarily be identical to that of the $U = 0$ system and it must then be different from the density of the original system. Again, the Kohn-Sham system proves incapable of simulating the reduction of the overlap.

C. Discussion

So far, we have proved that for small M as well as in the limit $M \to \infty$, the density of the interacting Hubbard chain is *not* noninteracting v representable. Although translational invariance is not strictly satisfied in the case of a finite chain length, from a physical point of view, the situation of an atom far from the ends, where surface effects have little influence, is no different from that of an atom in an infinite chain. It is thus not surprising that the Kohn-Sham system should approach the $U = 0$ system in the central region of the chain. In fact, this effect is already visible in the case of $M = 8$ and it should become even more dominant for greater M.

The argument concerning the limit $M \to \infty$ does not rely on the value of U and holds for any nonzero interaction. We have thus conclusively shown that the density of the interacting Hubbard chain is *not* noninteracting v representable for all values of M and U. Furthermore, the same argument can be used for regular lattices with nearest-neighbor hopping in dimensions other than one.

D. A semiconductor model

Another generalized model "with parameters more appropriate for a semiconductor" has been studied in Ref. 5. The eigenvalue gap obtained by density-functional theory that reproduced the occupation numbers correctly was shown to be in good agreement with the true band gap, whereas the value obtained by a LDA within that framework was much smaller. It was therefore concluded that the LDA rather than the discontinuity in the exchange-correlation potential seemed to be responsible for the numerical deviation found in DFT calculations, but doubts have been raised concerning the implications for the original formulation of density-functional theory.[14]

Mathematically, the semiconductor model is equivalent to a Hubbard Hamiltonian in the presence of a spin-dependent potential and with the possibility of spin flip-

ping. It features two nondegenerate orbitals, each of which forms its own energy band. The electrons can move within these bands as well as change from one to the other. The model is understood to represent a semiconductor without magnetic properties. Therefore, the electrons are regarded as spinless fermions and the energy levels are interpreted as a low-lying s band and a p band. All orbitals are considered localized, so that overlap is negligible except on the same site and between nearest neighbors. The two levels are labeled by $\alpha, \beta \in \{s, p\}$. For a finite one-dimensional chain, the Hamiltonian is given by

$$\begin{aligned}\hat{H} = &\sum_{i=1}^{M} \sum_{\alpha} e_{i\alpha} \hat{n}_{i\alpha} + \sum_{i=1}^{M} t_{is,ip} \left(c_{is}^{\dagger} c_{ip} + c_{ip}^{\dagger} c_{is} \right) \\ &+ \sum_{i=1}^{M-1} \sum_{\alpha,\beta} t_{i\alpha,(i+1)\beta} \left(c_{i\alpha}^{\dagger} c_{(i+1)\beta} + c_{(i+1)\beta}^{\dagger} c_{i\alpha} \right) \\ &+ \sum_{\alpha,\beta} t_{M\alpha,1\beta} \left(c_{M\alpha}^{\dagger} c_{1\beta} + c_{1\beta}^{\dagger} c_{M\alpha} \right) + U \sum_{i=1}^{M} \hat{n}_{is} \hat{n}_{ip}. \quad (24)\end{aligned}$$

The first term contains the on-site energies $e_{i\alpha}$, the second and third govern the hopping between orbitals at the same site and between nearest neighbors. Likewise, the following term has been introduced to connect the end sites. As the orbitals are no longer degenerate, all hopping parameters must depend both on spatial position and the energy bands involved. The last contribution to the Hamiltonian is the on-site Coulomb interaction.

The density-functional formalism derived for the Hubbard Hamiltonian can be applied with minor changes, which account for the fact that the two orbitals differ. In particular, we have to consider occupation numbers and overlap coefficients for each pair of orbitals separately:

$$n_{i\alpha,j\beta} = \langle \Psi | c_{i\alpha}^{\dagger} c_{j\beta} | \Psi \rangle \quad \text{or} \quad n_{i\alpha,j\beta} = \sum_{\gamma=1}^{N} \langle \psi_{\gamma} | c_{i\alpha}^{\dagger} c_{j\beta} | \psi_{\gamma} \rangle. \quad (25)$$

We take parameters for the interacting system from Ref. 5. The energy levels are $e_{is} = -4.0$ and $e_{ip} = 0.0$. At the end points, the s state is raised by 1.0 and the p state is lowered by 0.4 to simulate surface effects. There is no hopping between bands on the same site; the sign and the magnitude of the other hopping parameters are consistent with a picture of real symmetric s and antisymmetric p orbitals and set to $t_{is,(i+1)s} = -1.8$, $t_{ip,(i+1)p} = 1.0$, and $t_{is,(i+1)p} = -t_{ip,(i+1)s} = 1.2$. The end points are joined only by $t_{Ms,1p} = -t_{Mp,1s} = 1.2$. Finally, the interaction parameter is $U = 4.0$.

The symmetries of the chain are more subtle than in the Hubbard case. When varying the effective parameters in the one-particle Hamiltonian $\hat{H}_s$, we constrain $e_{i\alpha}^{\text{eff}} = e_{(M+1-i)\alpha}^{\text{eff}}$. Due to the different signs of the orbital lobes, the hopping parameters are related by $t_{is,ip}^{\text{eff}} = -t_{(M+1-i)s,(M+1-i)p}^{\text{eff}}$ and $t_{i\alpha,(i+1)\beta}^{\text{eff}} = \mp t_{(M-i)\beta,(M-i+1)\alpha}^{\text{eff}}$ with $-$ for $\alpha \neq \beta$ and $+$ otherwise. Likewise, at the end points, $t_{M\alpha,1\beta}^{\text{eff}} = -t_{M\beta,1\alpha}^{\text{eff}}$ for $\alpha \neq \beta$. The density coefficients are related by the very same symmetries. A measure for the accuracy of an approximation to the density is again given by the sum of squares *SUMSQ* taken over the deviations of all independent coefficients.

TABLE IV. Deviation between the independent density coefficients of the nine-site semiconductor chain and those of the Kohn-Sham system (KS), the noninteracting system with the same occupation numbers ($n_{i\alpha}$ exact), and the original system with interaction set to zero ($U = 0$), expressed through *SUMSQ* per site. Although the approximation becomes better with increasing M, the density of the interacting system is *not* noninteracting v representable.

M	KS	$n_{i\alpha}$ exact	$U = 0$
3	0.477×10^{-4}	2.331×10^{-4}	0.0379
5	0.118×10^{-4}	1.335×10^{-4}	0.0616
7	0.049×10^{-4}	1.006×10^{-4}	0.0759
9	0.034×10^{-4}	0.812×10^{-4}	0.0826

Calculated values of *SUMSQ* divided by the chain length M are listed in Table IV. The columns correspond to (i) the best-fit Kohn-Sham system, (ii) the system studied in Ref. 5, in which merely the on-site energies are varied so as to reproduce the occupation numbers of the original system exactly, and (iii) the noninteracting system with the same hopping parameters as the original interacting chain, which is used as the starting point for the numerical optimization.

Although *SUMSQ* assumes significantly lower values than it did for the Hubbard model, despite the sevenfold increase in density coefficients, it is still far from zero. For the chain lengths studied here, the density of this interacting semiconductor model is therefore *not* noninteracting v representable. To give an impression of the numerical deviations, Table V lists the density coefficients for the central site of the nine-site chain.

It seems that the approximation becomes better for increasing M, but the data are not sufficient for a reliable extrapolation. A formal repetition of our earlier argument regarding the limit $M \to \infty$ fails because translationally invariant systems will still retain five relevant hopping parameters that determine the density. On the other hand, particle conservation only helps to reduce the number of effectively independent density coefficients to six, so it seems probable that even in this limit the density is *not* noninteracting v representable. We have performed calculations for closed, translationally invariant ring chains up to $M = 9$ that are governed by the same ratio of significant hopping parameters and density coefficients. None of these systems was found to be noninteracting v representable.

To double-check these findings, we have also taken a completely different approach by varying the eigenvectors of the Hamiltonian matrix directly and without fur-

TABLE V. Density coefficients for the central site in a nine-site semiconductor chain. The columns correspond to the true interacting system ($U = 4$), the Kohn-Sham system (KS), the noninteracting system with the correct occupation numbers ($n_{i\alpha}$ exact), and the initial-guess system with interaction set to zero ($U = 0$).

	$U = 4$	KS	$n_{i\alpha}$ exact	$U = 0$
n_{5s}	0.9209	0.9215	0.9209	0.7021
n_{5p}	0.0782	0.0780	0.0782	0.2998
$n_{5s,5p}$	0.0000	0.0000	0.0000	0.0000
$n_{5s,6s}$	0.0360	0.0367	0.0363	0.1990
$n_{5p,6p}$	-0.0347	-0.0352	-0.0353	-0.2010
$n_{5s,6p}$	0.1641	0.1647	0.1671	0.2223
$n_{5p,6s}$	-0.1636	-0.1640	-0.1668	-0.2214

ther constraints. A Hamiltonian constructed in this way corresponds to the unphysical case of hopping not being restricted by distance. But although the number of variable hopping parameters grows exponentially with M, even the overlap between nearest neighbors cannot be reproduced accurately for $M \leq 7$. The formal inclusion of next-nearest-neighbor hopping in the Kohn-Sham system is therefore no solution.

V. CONCLUSION

We have reexamined the treatment of strongly correlated Hubbard-type models within density-functional theory. A formulation of the basic theorems that is related as closely as possible to the conventional scheme through second quantization of the external potential and the density has been provided. Numerical calculations and qualitative arguments have shown that the electron density of the original Hubbard model with nonzero interaction is *not* noninteracting v representable. The same result was found for a related semiconductor model that has been used in a study of the band-gap problem.

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